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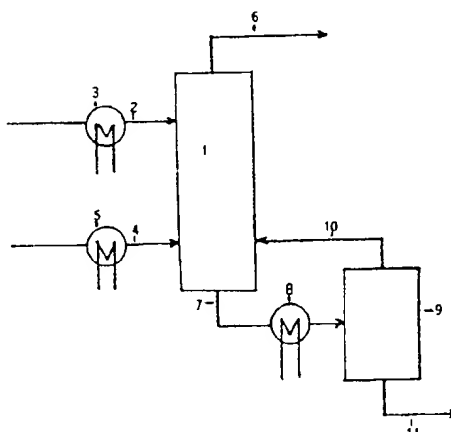
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7LN(GB)(54) **Process for the production of process oils with a low content of polycyclic aromatic compounds.**

(57) Process oils with an aromatic content of more than 50 weight %, in particular of more than 55 weight %, according to ASTM D 2007 and a content of polycyclic aromatic compounds of less than 3 weight % according to IP 346 are prepared from a primary extract (4) obtained by treatment of a lubricating oil distillate originating a mineral oil with a polar solvent. The primary extract (4) is extracted in a counter current extraction column (1) with a polar solvent (2) using a volume ratio of primary extract fed to the column to polar solvent in the range 1:1 to 1:1.8 as well as a temperature in the head region of the counter current extraction column in the range 50-90 °C and in the bottom region of 20-60 °C and with the head temperature higher than the bottom temperature.

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PROCESS FOR THE PRODUCTION OF PROCESS OILS WITH A LOW CONTENT OF POLYCYCLIC AROMATIC COMPOUNDS

The invention relates to a process for the production of process oils with an aromatic content of more than 50 weight %, in particular more than 55 weight %, according to ASTM D 2007 and with a content of polycyclic aromatics (PCA) of less than 3 weight % according to IP346.

Process oils are hydrocarbon mixtures boiling in the lubricating oil range which are not used as, or in connection with, lubricating oils but are used in other technological areas, e.g. as plasticisers or extenders. However the aromatic types frequently show undesirably high contents in polycyclic compounds, i.e. compounds containing more than 2 condensed, aromatic nuclei. When used as plasticisers in natural and synthetic rubber types, e.g. for rubber mixtures for the running surfaces of vehicle tires, they give an improvement in the physical properties of the rubber vulcanisate, especially with reference to the elasticity and the related property of wet grip of the running surface mixture. Other technical rubber articles plasticised with the above mentioned process oils show improved vibration damping properties.

The process oils of the above named type are described in German patent specification DE-A 23 43 238. They are there described as pseudo raffinate and are obtained as follows. A petroleum distillate boiling in the lubricating oil range is subjected to a counter current extraction with furfural, the resulting primary extract is freed from furfural and is again subjected to a second counter current extraction with furfural. The aromatic rich pseudo raffinate obtained in the second extraction step is freed from furfural and then treated with suitable solvents, e.g. methyl ethyl ketone and toluene, to remove wax and paraffin and finally catalytically hydrogenated. In the second extraction step the temperature at the head of the extraction column is in the range 40-100 °C and that in the bottom of the column is 35-80 °C. The volume ratio of the primary extract feed to the extraction solvent is in the range 1:0.5 to 1:2.5.

German patent specification DE-B 37 17 820 relates to a multi-stage extraction process with two counter current extraction columns and three or four separators. The process of DE-B 37 17 820 however is directed to the removal of aromatic components from the lubricating oil fraction fed to the process with optimisation of the yield of raffinate.

The process according to DE-A 23 43 238 produces process oils with a relatively low content in aromatic compounds, as a consequence of the required hydrogenation step. However process oils used as plasticisers or extenders for natural and synthetic rubber types frequently are required to have a high content in aromatic compounds. However the content in polycyclic aromatic compounds should be as low as possible, in particular under 3 weight %.

According to the present invention there is provided a process for the production of process oils with an aromatic content of more than 50 weight % according to ASTM D 2007 and a content of polycyclic aromatic compounds of less than 3 weight % according to IP 346 characterised in that primary extract, obtained by treatment of a lubricating oil distillate originating from a mineral oil, is extracted in a counter current extraction column with a polar solvent wherein the volume ratio of the primary extract feed to the polar solvent is in the range 1:1 to 1:1.8 and the head temperature in the counter current extraction column is 50-90 °C and the bottom temperature in the column is 20-60 °C and wherein the head temperature is higher than the bottom temperature.

The head temperature is to be understood as the temperature established in the uppermost part of the column (substantially depending on the feed temperature of the solvent and the primary extract stream) by which this can be controlled. It is practically identical with the temperature at which the product is taken off from the head of the column.

By bottom temperature of the column is to be understood the lowest temperature in the extraction process; it is principally dependent on the temperature of the two process feed streams mentioned above, but is however normally influenced or regulated by additional cooling installations in the bottom region of the column. The cooling installations can also be located outside the column and can be combined in this position with a separate separator, in which the product taken from the bottom of the column is separated into a heavier extract phase and a lighter phase, which is fed back into the bottom region of the column. This lighter phase is frequently designated as "pseudo raffinate". In this embodiment of the process of the invention the temperature ruling in the separator vessel and which is practically identical with that of the recirculated light phase represents the bottom temperature in accordance with the claims.

If the primary extract fed to the process contains small quantities of polar solvents (as a result of the process used to make it) then these must be taken into account in relation to the maintenance of the above mentioned limits for the ratio of primary extract to polar solvent. The content of residual solvent in the feed material is preferably not higher than 20 volume %.

According to an advantageous embodiment of the process of the invention a primary extract is fed which has an aromatic content of 65-85 weight % according to ASTM D 2007.

Usually the primary extract resulting from the extraction of lubricant distillate fractions contains 15-35 weight % of polycyclic aromatic compounds (PCA) according to IP 346; the content can however be above or below this range.

The preferred primary extracts for use in the process of the present invention have PCA contents of not more than 25 weight % according to IP 346. The lower limit of PCA-content of the primary extract for the process of the invention lies above the target PCA-content of the product of the process of the invention.

According to a further advantageous embodiment of the process of the present invention the head temperature in the counter current extraction column is at least 10 °C higher than the bottom temperature.

In this specification the term "polar solvents" is to be understood as covering the usual solvents used in the extraction of lubricating oil distillates, e.g. furfural, N-methylpyrrolidone and phenol; preferably furfural is used.

The process oil taken from the head of the counter current extraction column is freed, in particular by distillation, from quantities of polar solvent. Further processing of the process oil obtained in accordance with the invention by dewaxing and deparaffining is possible. However subsequent processing by hydrogenation is excluded from the process of the present invention, as the content in polycyclic aromatics in the process oil of the invention already lies under 3 weight % and hydrogenation would reduce the desired high content in non polycyclic, aromatic compounds.

For carrying out the process of the invention the usual columns for counter current liquid extraction, as described in Ullmann's Encyclopedia of Industrial Chemistry 5th Edition Volume B3 1988, pages 6-14 to 6-32; particular advantageous are columns with rotating elements, e.g. rotating disk contactors, RDCs.

The process oils obtained by the process of the invention may be used in the technological areas in which aromatic rich mineral oil extracts have been used up to now. In accordance with the invention they are preferably used as plasticisers or extenders for natural or synthetic rubber types, and as base oils for printing oil formulations.

The process of the invention will be further described below, with reference to the drawing. The drawing shows a flow sheet for a preferred installation for carrying out the process of the present invention.

According to the drawing an installation for carrying out the process of the invention comprises a counter current extraction column of usual type (1). Column (1) is connected by line (2) to a heat exchanger (3). A polar solvent is fed through heat exchanger (3) via line (2) into column (1).

Primary extract with an aromatic content of more than 50 weight % according to ASTM D 2007 and a content of polycyclic aromatic compounds of more than 3 weight % according to IP 346 is fed into column (1) through line (4), having previously passed through heat exchanger (5).

The process oil obtained according to the invention, hereinafter designated as "mesoraffinate", is taken off at the head of the column by line (6).

The polar solvent containing the extracted constituents is taken off from the base of the extraction column through line (7) and fed through heat exchanger (8) to a separator (9), where the extract separates into two phases. The upper phase, frequently designated as pseudo raffinate, is returned by line (10) to the base of the extraction column; the lower phase, containing the polar solvent and enriched in the undesired polycyclic aromatic compounds, is removed from the installation by line (11). The equipment for the removal and recovery of polar solvents from the process oil taken from the head of the column and from the base product containing the undesirable aromatic compounds are not shown.

The spatial separation of the extraction column (1) and the separator (9) is not essential; it is possible to integrate the separator (9) with the base of column (1).

The installation represented in the drawing allows a specially close control of the extraction procedure. It is however completely possible to work without the recycle through the heat exchanger (8), the separator (9) and the line (10). The process parameters characterising the process of the invention are then only controlled by the temperature of the two input streams and the quantities fed, which experience shows is not carried out so elegantly. The process of the invention will now be illustrated by reference to the following Examples.

A rotating disk contactor with a height of 4000 mm, and a diameter of 115mm and with 56 disks was used; the rate of rotation of the disks in all cases was 180 rpm. Furfural was used as the polar solvent; the quantity fed is indicated by the ratio of primary extract to furfural given in Table 2.

The starting material was an extract obtained as a by-product of the preparation of a normal solvent-neutral oil by distillation of North Sea crude oil and subsequent extraction with furfural. It had the following characteristics:

TABLE 1

Density at 70 °C (DIN 51557; kg/m ³)	956
Viscosity at 40 °C (DIN 51562; mm ² /s)	1530
Viscosity at 100 °C (DIN 51562; mm ² /s)	30.5
Refractive index n _D ²⁰ (DIN 51423/T2)	1.560
Flashpoint COC (°C; DIN ISO 2592)	255
Pourpoint (°C; DIN ISO 3016)	+ 18
Aromatic content (weight %; ASTM D 2007)	74
Polycyclic aromatics (weight %; IP 346)	19

Examples 1 to 3 of the invention as well as Comparative Tests A and B were carried out with the above starting material. The process conditions (temperature at the head of the column and at the base of the column and the volume ratio extract: furfural) and the experimental results (yield in mesoraffinate in weight %, calculated on the starting material, aromatic content of the meso raffinate in weight % according to ASTM D 2007 and content of polycyclic aromatic compounds (PCA-content) in weight % according to IP 346) are set out in Table 2.

As can be seen from the experiments the products of Examples 1 to 3 have aromatic contents of well below 60 weight %; the content of polycyclic aromatic compounds lies significantly below 3 weight %. The Comparative Test A shows that a column head temperature outside the claimed temperature range reduces the PCA-content but at the same time also reduces the aromatic content of the final product to below 50 weight %. The Comparative Test B shows that the use of a volume ratio of raffinate to furfural below that required by the claims leaves the aromatic content substantially unaffected but leaves the PCA content however at an undesirably high level.

A further comparison of the results obtainable with the process of the invention with the state of the art shows that according to Example 1, extract A of DE-A 23 43 238 has an aromatic content of the process oil before dewaxing and hydrogenation of 71.8 weight % and after the dewaxing and hydrogenation has an aromatic content of 51.9 %. The corresponding values for the extract B obtained in Example 2 of DE-A 23 43 238 are 65.7 weight % and 51.1 weight % after hydrogenation.

The PCA-contents obtainable according to DE-A 23 43 238 can not now be established, as the starting material used in this specification can no longer be obtained. (In any case the process according to DE-A 23 43 238 must be regarded as disadvantageous, as it requires an additional hydrogenation step, through which the content in aromatics is substantially reduced).

Table 2 now follows:

TABLE 2

	COLUMN HEAD °C	COLUMN BASE °C	PRIMARY EXTRACT: FURFURAL	MESORAFFINATE YIELD WEIGHT%	AROMATIC CONTENT WEIGHT %	PCA CONTENT WEIGHT %
Invention						
Example 1	70	35	1 : 1.5	51	70.2	2.1
Example 2	77	41	1 : 1.5	34	67.2	1.9
Example 3	88	45	1 : 1.5	31	66.5	1.2
Comparative Text A	100	55	1 : 1.5	15	44.3	0.6
Comparative Text B	65	38	1 : 0.55	75	70.1	9.6

° Temperature of the separator
Throughput of primary extract 5 kg/h

Claims

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1. Process for the production of process oils with an aromatic content of more than 50 weight % according to ASTM D 2007 and a content of polycyclic aromatic compounds of less than 3 weight % according to IP 346 characterised in that primary extract, obtained by treatment of a lubricating oil distillate originating from a mineral oil, is extracted in a counter current extraction column with a polar solvent wherein the volume
10 ratio of the primary extract feed to the polar solvent is in the range 1:1 to 1:1.8 and the head temperature in the counter current extraction column is 50-90 °C and the bottom temperature in the column is 20-60 °C and wherein the head temperature is higher than the bottom temperature.
2. Process according to claim 1 characterised in that the extract fed to the process has an aromatic content of 65-85 weight % according to ASTM D 2007.
- 15 3. Process according to claim 1 or 2, characterised in that the extract fed to the process has a content of polycyclic aromatic compounds according to IP 346 of not more than 25 weight %.
4. A process according to any one of claims 1 to 3 characterised in that the head temperature of the counter current extraction column is at least 10 °C higher than the bottom temperature.
5. Process according to any one of claims 1 to 4 characterised in that furfural is used as the polar solvent.
- 20 6. Process according to any one of claims 1 to 5 characterised in that the process oil taken from the head of the counter current extraction column is freed from polar solvents.
7. Use of a process oil obtained according to any one of claims 1 to 6 as a plasticiser or extender for natural and synthetic rubber types, and as a base oil for printing oil formulations.

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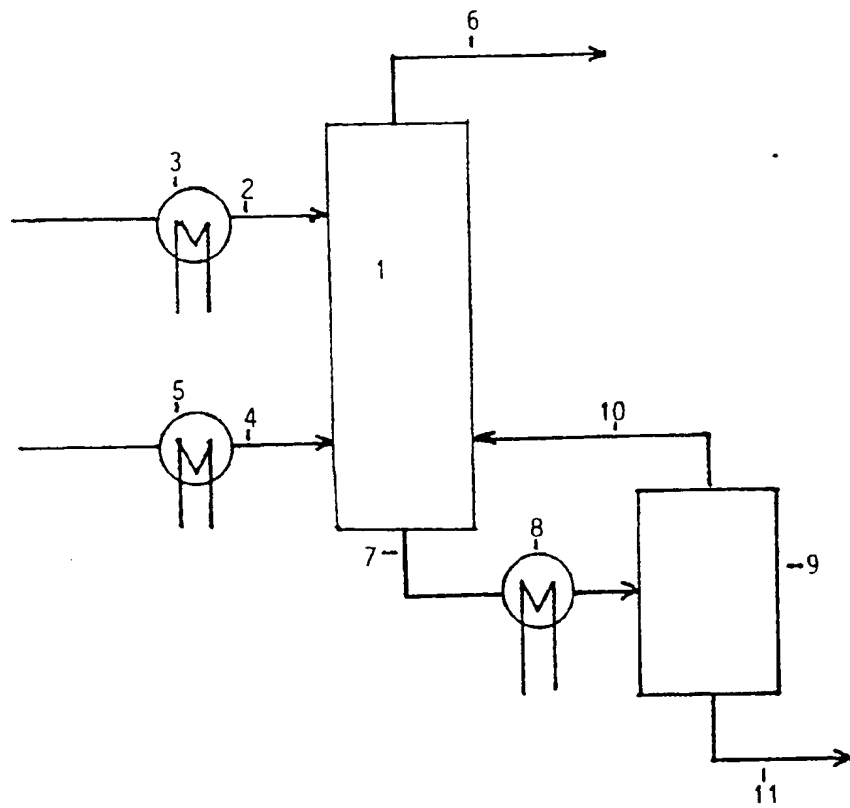
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EUROPEAN SEARCH REPORT

Application Number

EP 90 30 9772

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
D,A	DE-A-2 343 238 (BRITISH PETROLEUM CO.) * Claims 1,8,10; page 1, paragraph 1 * -----	1,5,7	C 10 G 21/00
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			C 10 G
The present search report has been drawn up for all claims			
Place of search		Date of completion of search	Examiner
The Hague		19 November 90	DE HERDT O.C.E.
<div>CATEGORY OF CITED DOCUMENTS</div> <div><div>X: particularly relevant if taken alone Y: particularly relevant if combined with another document of the same category A: technological background O: non-written disclosure P: intermediate document T: theory or principle underlying the invention</div><div>E: earlier patent document, but published on, or after the filing date D: document cited in the application L: document cited for other reasons &: member of the same patent family, corresponding document</div></div>			